

## Theory of the splitting and line shape of fluorescence for a magnetic impurity in a magnetic matrix with application to $\text{Cr}^{3+}$ in $\text{GdAlO}_3$

J. S. Helman

*Departamento de Física, Centro de Investigación del Instituto Politécnico Nacional, Apartado Postal 14-740, México, D.F. 07000, México*

W. Baltensperger

*Theoretische Physik, Eidgenössische Technische Hochschule, Zürich 8093, Switzerland*  
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The interpretation of the fluorescence spectrum of a magnetic impurity ion exchange-coupled to a magnetic matrix is reconsidered with a theory which incorporates correlation between the impurity spin and the neighboring ion spins and the concept of a Frank-Condon principle for the magnetic state. Line shapes and splittings are calculated as functions of temperature and magnetic field for an antiferromagnetic matrix. The application of the results to the Cr-doped  $\text{GdAlO}_3$  system removes inconsistencies of previous interpretations.

### INTRODUCTION

The present paper proposes a theory for a magnetic impurity coupled to an antiferromagnetic matrix. An example of such a system which has been studied in detail experimentally is a  $\text{Cr}^{3+}$  impurity in  $\text{GdAlO}_3$ . In this lattice  $\text{Cr}^{3+}$  substitutes  $\text{Al}^{3+}$  in the center of a slightly deformed cube, the vertices of which are occupied by Gd ions. The oxygen ions are at the centers of the faces of the cube. The magnetic phase diagram has been determined by Blazey *et al.*<sup>1,2</sup> The luminescence and optical absorption have been measured extensively by Murphy and Ohlmann,<sup>3</sup> Blazey and Burns,<sup>4</sup> Helman *et al.*,<sup>5</sup> and Aegerter *et al.*<sup>6</sup> Here we are mainly concerned with the line shapes and splittings of the fluorescence spectra. In the paramagnetic region broad lines are observed with an almost temperature-independent splitting of  $20 \text{ cm}^{-1}$  between the Néel temperature at 3.8 K and room temperature. Below the Néel temperature the splitting initially decreases linearly and then appears to level off at around  $11 \text{ cm}^{-1}$ . A magnetic field increases the splitting, which, however, saturates together with the magnetization of the Gd matrix.

The high-temperature splitting and line shapes have been explained<sup>3,4</sup> as being induced by the fields of all possible arrangements of the eight spins  $\frac{7}{2}$  of the Gd ion nearest to Cr. This leads to an exchange coupling constant of absolute value  $2.1 \text{ cm}^{-1}$  between a Gd spin and the spin of Cr in the ground state under the assumption that the

fluorescence comes from a single excited state. However, with this value of the exchange coupling, the Cr ion is able to order ferromagnetically the neighboring Gd ions, which leads to an increased splitting at low temperatures, contrary to the observations in luminescence,<sup>4,7</sup> which indicate that the cluster of Gd neighbors is antiferromagnetically ordered. A previous attempt to reconcile these apparently conflicting facts<sup>7</sup> was left with the stability problem that the state considered had a higher free energy than the ferromagnetic cluster. An extension of that theory into the paramagnetic region with magnetic field suffers from the same inconsistency.

The present paper shows that a consistent picture can be reached with the introduction of two new features. The Frank-Condon principle is extended to the magnetic states of the Gd cluster in the sense that during the luminescent transition the magnetic order of the cluster remains unchanged and is determined by the matrix with the Cr in the excited state. The stability of the observed antiferromagnetic state therefore requires only that the exchange coupling constant in the excited state of Cr is sufficiently small.<sup>8</sup>

With an antiferromagnetically ordered cluster, the question<sup>4,7</sup> remains; Why does the splitting not extrapolate to zero with decreasing temperature? A correlated wave function is proposed for the impurity and cluster spins, which leads to a finite splitting at low temperatures. Both line shapes and splitting are evaluated as functions of temperature

and magnetic field. For high fields the splitting saturates. The calculations are, however, only performed for a spin- $\frac{1}{2}$  impurity, which limits a detailed comparison with experiment.

### THE MODEL

The model proposed here may have wide applications; however, to fix the ideas, we consider the case of Cr-doped GdAlO<sub>3</sub>, where Cr is a substitutional impurity at an Al site. Its spin interacts with the spins of a cluster of eight Gd neighbors. These in turn are coupled to the antiferromagnetic matrix and among themselves.

The spin Hamiltonian is of the form

$$H = H_A + H_C + J \vec{s} \cdot \sum_{j=1}^8 \vec{S}_j - g \mu_B \vec{B} \cdot \vec{s}. \quad (1)$$

$H_A$  describes the exchange coupling of the Gd cluster with the outside antiferromagnetic medium and the outside magnetic field,

$$H_A = \sum_{j=1}^8 \vec{S}_j \cdot \left[ I \sum_l \langle \vec{S}_l \rangle_{T,B} - g' \mu_B \vec{B} \right]. \quad (2)$$

Here  $\vec{S}_j$  is a cluster spin, while  $\vec{S}_l$  belongs to the outside matrix. Since the treatment of the outside matrix is not the main concern of this paper, we shall describe its effect by a thermodynamic average over the matrix states.  $H_A$  therefore represents the action of a temperature- and magnetic-field-dependent Weiss field on the clusters spins.

$H_C$  contains the interactions within the cluster

$$H_C = \sum_{(j,k)} I' \vec{S}_j \cdot \vec{S}_k, \quad (3)$$

where the sum extends over the twelve nearest-neighbor links. The exchange integral  $I'$  may differ from that of the matrix,  $I$ , in view of the presence of the impurity. In order to have as few parameters as possible, we shall assume  $I' = I$  in the following.

The third term describes the exchange interaction between the spins  $\vec{S}_j$  of the Gd ions of the cluster with the spin  $\vec{s}$  of the Cr impurity. The last term is the Zeeman energy of the Cr impurity.

The outside Gd matrix will enter the theory in a molecular field approximation. Since fluctuations in the cluster will play an essential role, this requires a microscopic treatment. Since, however, there are eight spins  $\frac{7}{2}$  besides the Cr spin, an exact diagonalization is not feasible. We therefore make use of an ansatz<sup>7</sup> for a typical cluster wave

function in the temperature ensemble

$$|\psi\rangle = \prod_{j=1}^8 \sum_{n=0}^{2S} A_{nj} |S-n\rangle_j, \quad (4)$$

where

$$A_{nj} = \left[ \binom{2S}{n} P_j^n (1-P_j)^{2S-n} \right]^{1/2} e^{in\theta_j}, \quad (5)$$

with

$$P_j = (S - \Sigma_j) / 2S. \quad (6)$$

$|S-n\rangle_j$  are eigenfunctions of  $S_j^z$ ,

$$S_j^z |S-n\rangle_j = (S-n) |S-n\rangle_j. \quad (7)$$

For each set of values of the parameters  $\Sigma_j$  and  $\theta_j$  ( $j=1, \dots, 8$ ),  $|\psi\rangle$  describes a spin state of the cluster of eight Gd ions around the Cr spin. Note that  $|\psi\rangle$  is not an eigenstate of the total spin or its  $z$  component. The form chosen for  $|\psi\rangle$  allows an easy calculation of matrix elements, in particular,  $\langle \psi | \psi \rangle = 1$  and

$$\langle \psi | S_j^z | \psi \rangle = \Sigma_j, \quad (8)$$

$$\langle \psi | S_j^\pm | \psi \rangle = (S^2 - \Sigma_j^2)^{1/2} e^{\pm i\theta_j}. \quad (9)$$

Other useful matrix elements are given in the Appendix. The physical meaning of the parameters  $\Sigma_j$  and  $\theta_j$  as quantum-mechanical mean values is apparent from Eqs. (8) and (9). However, they are not uniquely determined by the knowledge of the thermodynamic state of the cluster. Thus, they will be treated as random variables with two conditions on their distribution functions: (i) Their mean values must coincide with those given by a mean-field theory of the magnetic state of the cluster, and (ii) their fluctuations must be within physically allowed ranges. [Examples are given by Eqs. (27) and (30).]

The ground state of Cr<sup>3+</sup> in a cubic crystal field is an <sup>4</sup>A quadruplet, which splits into two Kramers doublets in the presence of a trigonal deformation. Actually, this splitting is smaller than the terms considered in the Hamiltonian and it will be neglected.

We shall now discuss the correlation between the Cr spin and the cluster spins. The method becomes quite cumbersome with four Cr states. For this reason we shall consider a spin- $\frac{1}{2}$  impurity only.

The exchange coupling between the impurity spin and the cluster spins leads to mutual spin flips. Therefore, if these correlations are to be incorporated into the theory, the cluster state cannot

be described by a single function  $|\psi\rangle$  with a fixed set of parameters, as was done in a previous treatment.<sup>7</sup> Thus at least one further cluster state must be considered. With the idea of spin flips in mind we introduce the symmetric spin-wave state:

$$|\chi^+\rangle = \alpha \sum_{j=1}^8 S_j^+ |\psi\rangle, \quad (10)$$

with

$$\alpha^{-2} = \left\langle \psi \left| \sum_{j,k} S_j^- S_k^+ \right| \psi \right\rangle. \quad (11)$$

We therefore treat the problem in the space of the two states

$$|\psi, \uparrow\rangle, \quad |\chi^+, \downarrow\rangle, \quad (12)$$

where the arrow refers to the  $z$  component of the impurity spin. Obviously,  $\langle \chi^+, \downarrow | \psi, \uparrow \rangle = 0$ . For an impurity spin larger than  $\frac{1}{2}$ , further magnon states must be introduced.

There is an asymmetry in these definitions, since  $|\chi^+\rangle$  has added angular momentum in the  $+z$  direction. This becomes most manifest when  $|\psi\rangle$  is fully spin polarized in the  $+z$  direction, in which case  $|\chi^+\rangle$  does not exist. In order not to lose the correlation with this choice of wave func-

tion, we shall introduce magnetic fields which polarize in the  $-z$  direction.

An equally justified choice of two states would be

$$|\tilde{\psi}, \downarrow\rangle, \quad |\chi^-, \uparrow\rangle = \alpha' \sum_{j=1}^8 S_j^- |\tilde{\psi}, \downarrow\rangle. \quad (13)$$

In the absence of magnetic fields these states are the time reversed of the states (12). The spectra of the two treatments then coincide due to the Kramers theorem.

Let  $E$  be the diagonal cluster energy

$$\langle \psi | (H_A + H_C) | \psi \rangle = E, \quad (14)$$

and  $\hbar\Omega$  the diagonal spin-wave energy,

$$\langle \chi^+ | (H_A + H_C) | \chi^+ \rangle = E + \hbar\Omega. \quad (15)$$

The components of the total cluster spin

$$R^z = \sum_{j=1}^8 S_j^z, \quad R^\pm = \sum_{j=1}^8 S_j^\pm \quad (16)$$

and products of these operators have matrix elements listed in the Appendix.

The energy matrix in the space of the states  $|\psi, \uparrow\rangle, |\chi^+, \downarrow\rangle$  reads

$$\begin{pmatrix} E + \frac{1}{2}JR_\psi^z - \frac{1}{2}g\mu_B B^z & \frac{1}{2}J\alpha(R^-R^+)_\psi - \frac{1}{2}g\mu_B\alpha B^+R_\psi^- \\ \frac{1}{2}J\alpha(R^-R^+)_\psi - \frac{1}{2}g\mu_B\alpha B^-R_\psi^+ & E + \hbar\Omega - \frac{1}{2}J\alpha^2(R^-R^2R^+)_\psi + \frac{1}{2}g\mu_B B^z \end{pmatrix}, \quad (17)$$

where  $B^\pm = B^x \pm iB^y$ . The subindex  $\psi$  refers to the quantum mechanical expectation value of the operator in the state  $|\psi\rangle$ . The secular equation has two roots:

$$\begin{aligned} \omega_\pm = & E + \frac{1}{2}(\hbar\Omega - \frac{1}{2}J\delta) \\ & \pm \frac{1}{2} \left[ \left( \frac{1}{2}J\delta - \hbar\Omega + JR_\psi^z - g\mu_B B^z \right)^2 \right. \\ & \left. + \left| \frac{J}{\alpha} - g\mu_B\alpha B^+R_\psi^- \right|^2 \right]^{1/2}, \quad (18) \end{aligned}$$

with

$$\delta = \alpha^2(R^-R^2R^+)_\psi - R_\psi^z. \quad (19)$$

The splitting is given by

$$\epsilon = \omega_+ - \omega_-. \quad (20)$$

The quantity  $\delta$  is the difference in the  $z$  component of the cluster spin in the states  $|\psi\rangle$  and  $|\chi^+\rangle$ . For a spin wave one would expect this to

be equal to one. Note, however, that  $|\psi\rangle$  usually contains an amplitude of maximum  $+z$  polarization. For this reason the calculated expression given in the Appendix is rather complicated. It decreases from one as  $|\psi\rangle$  approaches the ferromagnetic state in the  $+z$  direction.

The quantity  $\hbar\Omega$  is more difficult to calculate, since it involves the expectation value of products of four spin operators. Conceptually, it is the energy of a spin wave localized in the cluster. It will depend on temperature and polarization and it contains a Zeeman term proportional to  $\delta$ :

$$\hbar\Omega = a(T, B) - g'\mu_B B^z \delta. \quad (21)$$

Since  $\delta$  is usually one and  $g' = g$ , this Zeeman term cancels the corresponding term due to the impurity spin in the splitting (20). This is due to the fact that the two states  $|\psi, \uparrow\rangle, |\chi^+, \downarrow\rangle$  have almost the same total  $z$  component of spin. The magnetic field only affects the energy by suppressing the correlation between the impurity and the cluster

spins.

From Eqs. (14) and (15),

$$a(B, T) = a_A + a_C, \quad (22)$$

where

$$a_A = \langle \chi^+ | H'_A | \chi^+ \rangle - \langle \psi | H'_A | \psi \rangle \quad (23)$$

and

$$a_C = \langle \chi^+ | H_C | \chi^+ \rangle - \langle \psi | H_C | \psi \rangle. \quad (24)$$

Here  $H'_A$  equals  $H_A$  for  $B=0$ . The expressions for  $a_A$  and  $a_C$  as functions of the parameters of the

state (4) are given in the Appendix. For  $I=I'=0.1 \text{ cm}^{-1}$ ,  $a(B, T) \lesssim 6SI = 2.1 \text{ cm}^{-1}$  in every case. Thus,  $a(B, T)$  is numerically insignificant for our purposes and it has been neglected in the calculations of the spectra.

This calculation approximates the ground state, as long as the exchange field of the cluster exceeds the Zeeman field on the impurity spin. At very large magnetic fields the state in which both the impurity spin and the cluster spins are aligned to the magnetic field becomes the ground state. This occurs when  $g\mu_B B^z > 8JS$  or for  $B^z > 67 \text{ T}$ .

### THE PARAMAGNETIC REGION, $B=0$

The exchange coupling constant  $J$  between the impurity and the cluster spins can be obtained from the high-temperature limit with  $B=0$ ; the spins of the cluster and the matrix are then disordered. Thus,

$$\epsilon = JSf, \quad (25)$$

$$f = \left[ \left( \frac{\delta}{2} + R_\psi^z \right)^2 + \left| \frac{1}{\alpha} \right|^2 \right]^{1/2} / S$$

$$= \left[ \left( \frac{\delta}{2} + \sum_j \Sigma_j \right)^2 + \left| \sum_j (S^2 - \Sigma_j^2)^{1/2} e^{i\theta_j} \right|^2 + \sum_j \frac{(S - \Sigma_j)^2}{2S} \right]^{1/2} / S. \quad (26)$$

In the high-temperature limit  $\Sigma_j$  and  $\theta_j$  are continuous random variables in the ranges  $-\frac{7}{2} \lesssim \Sigma_j \lesssim \frac{7}{2}$  and  $-\pi \lesssim \theta_j \lesssim \pi$ . Here  $a_A + a_C$  has been neglected. The resulting statistical distribution function  $P(f)$  is given in Fig. 1.

Since  $\omega_{\pm} - E = \pm sSJf$ , the high-temperature line shape is given by Fig. 1, completed with the mirror

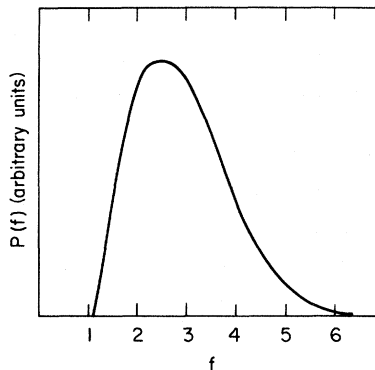


FIG. 1. Distribution function of  $f$ , in the high-temperature limit. The splitting is given by  $JSf$ .

image for negative  $f$ , where the abscissa is scaled by  $\frac{1}{2}JS$ . The peak of  $P(f)$  is at  $f_{\max} = 2.56$ , which is close to  $\sqrt{8}$ . This corresponds to the field of a random addition of eight spins. When  $f < 1.1$ ,  $P(f)$  becomes negligible. Even a fully antiferromagnetic state  $|\psi\rangle$ , where four of the  $\Sigma_j$  are  $+S$  and four are  $-S$ , leads to a splitting, owing to the correlations between the impurity and the cluster spins.

A comparison with the experiments is faced with the problem that  $\text{Cr}^{3+}$  has spin  $\frac{3}{2}$ . Since the treatment given for spin  $\frac{1}{2}$  has been able to account for statistical and correlation effects, it is anticipated that a corresponding calculation for spin  $\frac{3}{2}$  will simply add two more states. This assumption is supported by the results of the exact diagonalization which can be carried out for impurity spins  $\frac{1}{2}$  and  $\frac{3}{2}$  in the case of noninteracting cluster spins<sup>3</sup>; it is found that the density of states has two and four slightly asymmetric peaks, respectively. Thus, neglecting a possible asymmetry, an approximate density of states can be obtained from  $P(f)$  of Fig. 1 as  $D = P(3f) + \frac{1}{3}P(f)$ . This density of

states is given in Fig. 2.

The general shape is similar to the density of states obtained by Blazey and Burns<sup>4</sup> who evaluated the mean field produced by the Gd ions, in random orientations. The essential difference is the gap around  $E$ , which is due to the correlation between the impurity and the Gd spins. Identifying the high-temperature experimental splitting of  $\epsilon = 20 \text{ cm}^{-1}$  with the calculated distance between peak positions  $\epsilon = JSf_{\text{max}}$  with  $f_{\text{max}} = 2.56$ , the value  $|J| = 2.23 \text{ cm}^{-1}$ , is obtained. This value agrees with earlier estimates,<sup>3,4,7</sup> and it has been pointed out that such a large coupling between Cr and the Gd cluster results in a ferromagnetic order of the cluster in the ground state.

THE ANTIFERROMAGNETIC REGION

The experimental evidence is that the splitting is constant above the Néel temperature ( $T_N = 3.8 \text{ K}$ ) and decreases when the temperature drops below  $T_N$  (Fig. 3). This is only possible if the cluster essentially follows the antiferromagnetic behavior of the matrix and does not go into a ferromagnetic state.<sup>4,7</sup> This leads us to postulate a Frank-Condon principle for the magnetic state of the cluster. This means that the polarization of the cluster is constant during the luminescent transition and that it is determined by the luminescent excited state of the Cr ion interacting with the matrix. In order to account for the observed antiferromagnetic state of the cluster, we therefore assume that the exchange coupling constant of the excited Cr ion is sufficiently small.<sup>8</sup>

With Eq. (26) for  $f$ , a sublattice magnetization

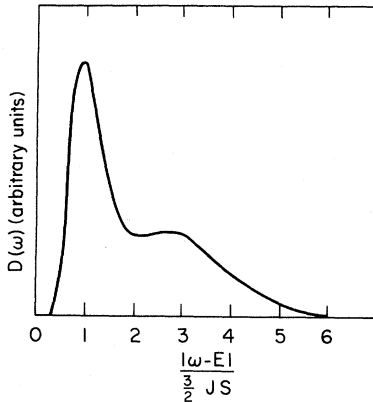


FIG. 2. Density of states for an impurity spin  $\frac{3}{2}$  in the high-temperature limit. The figure is to be completed with the mirror image for negative  $\omega - E$ .

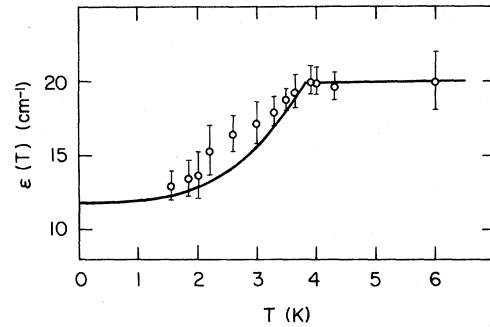


FIG. 3. Splitting as a function of temperature. Experimental points from Ref. 4 and theory (solid line).

$\sigma_s$  can be simulated using for the random variables  $\Sigma_j$  the form

$$\Sigma_j = (-1)^j \sigma_s + (S - \sigma_s)(1 - 2x_j), \tag{27}$$

where  $x_j$  ( $j = 1, \dots, 8$ ), is a set of random variables between 0 and 1.  $\sigma_s$  is calculated by mean-field theory as a function of temperature using a single exchange constant  $I' = I$  and the experimental value of  $T_N$  for the matrix. In Fig. 3 the experimental splitting as a function of temperature is compared with this calculation. The fact that the experimental points are higher may be due to a slight magnetization of the cluster induced by the excited Cr ion. The agreement at low temperatures shows that even with maximum sublattice magnetization the correlation provides the observed splitting. Figure 4 shows line shapes at  $T = 3, 2,$  and  $0 \text{ K}$ .

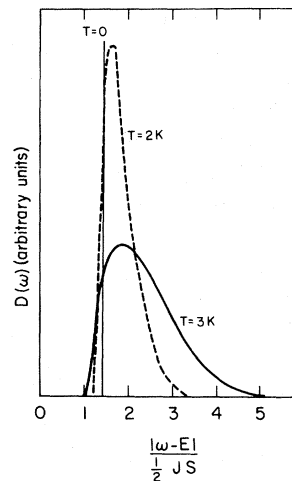


FIG. 4. Calculated density of states in the antiferromagnetic region for  $T = 3, 2,$  and  $0 \text{ K}$ .

### MAGNETIC-FIELD DEPENDENCE IN THE PARAMAGNETIC REGION

With a magnetic field  $B^z$  which produces a spin polarization  $-S \lesssim \sigma \lesssim 0$ , the splitting becomes [from (18) and (20)]:

$$\epsilon = \left[ \left( \frac{J\delta}{2} + JR_{\psi}^z - a_A - a_C \right)^2 + |J/\alpha|^2 \right]^{1/2}. \quad (28)$$

Using the expressions for  $R_{\psi}^z$  and  $|\alpha|^2$  given in the Appendix and neglecting  $a_A + a_C$ , this becomes

$$\epsilon = \left[ \left( \frac{J\delta}{2} + J \sum_j \Sigma_j \right)^2 + J^2 \left[ \left| \sum_j (S^2 - \Sigma_j^2) e^{i\theta_j} \right|^2 + \sum_j \frac{(S - \Sigma_j)^2}{2S} \right] \right]^{1/2}. \quad (29)$$

The random variable  $\Sigma_j$  is now simulated by

$$\Sigma_j = \sigma + (S - |\sigma|)(1 - 2x_j), \quad (30)$$

where again the  $x_j$  ( $j=1, \dots, 8$ ) are a set of random numbers in the range  $0 \lesssim x_j \lesssim 1$ . The  $\theta_j$  are random in the interval  $-\pi \lesssim \theta_j \lesssim \pi$ . No effect of the impurity on the magnetization of the cluster is considered, since by the Frank-Condon principle this is established while the impurity is in the excited state, for which the exchange coupling constant is assumed to be small.

The theory which uses the time-reversed states  $|\psi \downarrow\rangle, |\chi^{-}\uparrow\rangle$  gives identical energy levels in the absence of a magnetic field, since it is irrelevant whether the spin wave used to produce a correlated wave function for the impurity and the cluster states have angular momentum in the  $+z$  or the  $-z$  direction. In the presence of a magnetic field an asymmetry appears, although the Zeeman term has canceled out if  $g=g'$  and  $\delta=1$ . The remaining difference is due to the fact that a spin wave of given angular momentum is gradually suppressed as the magnetization saturates in that direction. The splitting for the time-reversed calculation can be obtained from (29) using the opposite direction for the magnetic field. The difference is of order  $a_A + a_C$  at most.

Figure 5 shows line shapes at  $T=4.2$  K for several values of the magnetic field. Figure 6 gives the peak splitting at 4.2 K as a function of the magnetic field. The experimental values<sup>5</sup> of the

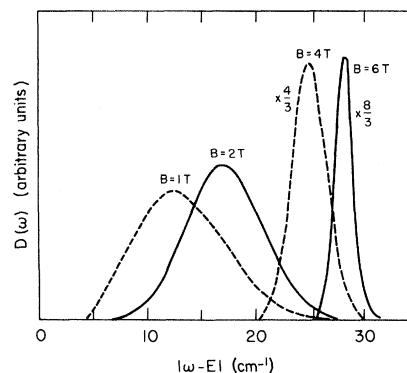


FIG. 5. Density of states for various magnetic fields in the paramagnetic region (4.2 K).

average splittings of the four largest peaks for Cr impurity in  $\text{GdAlO}_3$  has a similar behavior. However, the splitting reaches a saturation value at  $40 \text{ cm}^{-1}$ . At present we cannot account for this discrepancy of 30% at high fields. A possible reason is that the theory refers to a spin- $\frac{1}{2}$  impurity and cannot be simply applied to the spin- $\frac{3}{2}$  case.

In a previous paper<sup>5</sup> a phenomenological theory was used to interpret these data. The excellent agreement found was, however, fortuitous for two compensating reasons. Firstly, the data for the magnetization<sup>1</sup> referred to an adiabatic situation, as was pointed out later by Blazey *et al.*<sup>2</sup> Secondly, the phenomenological theory included a Zeeman energy, which we have now shown to cancel out. The saturation of the splitting found with the present theory is indeed a striking feature of the empirical spectra,<sup>9</sup> which show a constant splitting for fields from 4 to 6 T particularly at lower temperatures, where the cluster is nearly fully magnetized.

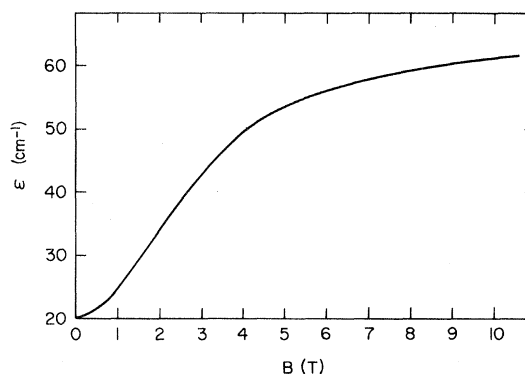


FIG. 6. Splitting as a function of magnetic field at 4.2 K.

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## APPENDIX

The following are useful matrix elements and formulas:

$$(S_j^z)_\psi = \Sigma_j, \quad (\text{A1})$$

$$[(S_j^z)^2]_\psi = \Sigma_j^2 + T_j^2/2S, \quad (\text{A2})$$

$$[(S_j^\pm)^m]_\psi = \frac{(2S)!}{(2S-m)!} \left( \frac{T_j}{2S} \right)^m e^{\pm im\theta_j} \quad \text{for } m=0,1,\dots,2S \quad (\text{A3})$$

$$(S_j^+ S_j^-)_\psi = T_j^2 + (S + \Sigma_j)^2/2S = (S_j^- S_j^+)_\psi + 2\Sigma_j, \quad (\text{A4})$$

$$(S_j^- S_j^z)_\psi = \left[ \Sigma_j + \frac{S - \Sigma_j}{2S} \right] T_j e^{-i\theta_j}, \quad (\text{A5})$$

$$\begin{aligned} [(S_j^z)^3]_\psi &= \Sigma_j^3 + \frac{3S-1}{2S^2} T_j^2 \Sigma_j \\ &= [(S_j^z)^2]_\psi \Sigma_j + \frac{2S-1}{2S^2} T_j^2 \Sigma_j, \end{aligned} \quad (\text{A6})$$

$$(S_j^- S_j^+ S_j^z)_\psi = (S_j^- S_j^+)_\psi \Sigma_j - \frac{T_j^2}{2S} \left[ 1 + \frac{2S-1}{S} \Sigma_j \right], \quad (\text{A7})$$

$$(S_j^- S_j^+ S_j^+)_\psi = (2S-1)(S - \Sigma_j) \left[ 1 - \frac{S-1}{2S^2} (S - \Sigma_j) \right] T_j e^{i\theta_j}, \quad (\text{A8})$$

$$\begin{aligned} (R^- R^+)_\psi &\equiv \alpha^{-2} = \left| \sum_j T_j e^{i\theta_j} \right|^2 + \sum_j (S - \Sigma_j)^2/2S \\ &= \sum_{j,k} T_j T_k \cos(\theta_j - \theta_k) + \sum_j (S - \Sigma_j)^2/2S, \end{aligned} \quad (\text{A9})$$

$$(R^z)_\psi^2 = \left[ \sum_j \Sigma_j \right]^2 + \sum_j T_j^2/2S, \quad (\text{A10})$$

$$\delta = 1 - \alpha^2 \left[ \sum_{j,k} \frac{\Sigma_k}{S} T_j T_k \cos(\theta_j - \theta_k) + \sum_j T_j^2 \frac{S - \Sigma_j}{2S^2} \right], \quad (\text{A11})$$

$$a_A/I = \sum_{(l,j)} \langle S_l^z \rangle_{T,B} f_j, \quad (\text{A12})$$

with

$$f_j = \alpha^2 \left[ T_j \left[ 1 - \frac{\Sigma_j}{S} \right] \sum_n T_n \cos(\theta_n - \theta_j) - \frac{(S - \Sigma_j)^2}{2S^2} \Sigma_j \right], \quad (\text{A13})$$

$$a_C/I' = -\alpha^2 \sum_{(j,k)} \left\{ \begin{aligned} & \frac{4S-1}{2S^2} T_j^2 T_k^2 \cos^2(\theta_j - \theta_k) \\ & + \frac{1}{2S^2} T_j T_k \cos(\theta_j - \theta_k) [(S - \Sigma_j)(S - \Sigma_k) - (2S - 1)(\Sigma_j - \Sigma_k)^2] \\ & + \frac{1}{2S} (T_j^2 \Sigma_k + T_k^2 \Sigma_j) - (S^2 - \Sigma_j \Sigma_k) \left[ 1 + \frac{2S-1}{2S^2} (T_j^2 + T_k^2) \right] - \sum_{\substack{n=1 \\ n \neq j \\ n \neq k}}^8 W_{n,j,k} \end{aligned} \right\}, \quad (\text{A14})$$

$$W_{n,j,k} = \frac{T_n}{2S} \{ (S^2 + \Sigma_k^2 - 2\Sigma_k \Sigma_j) T_j \cos(\theta_n - \theta_j) + (S^2 + \Sigma_j^2 - 2\Sigma_k \Sigma_j) T_k \cos(\theta_n - \theta_k) \\ - T_j T_k [T_j \cos(\theta_n + \theta_k - 2\theta_j) + T_k \cos(\theta_n + \theta_j - 2\theta_k)] \}, \quad (\text{A15})$$

$$a_C/I' = \alpha^2 \sum_{(j,k)} \left\{ \begin{aligned} & \sum_{n=1}^8 W_{n,j,k} - \frac{T_j T_k}{2S^2} \cos(\theta_j - \theta_k) [(S - \Sigma_j)(S - \Sigma_k) + (\Sigma_j - \Sigma_k)^2] \\ & + \frac{T_j^2 T_k^2}{2S^2} \cos^2(\theta_j - \theta_k) + \frac{1}{2} (\Sigma_j - \Sigma_k)^2 - \frac{T_j^2}{2S^2} \Sigma_k (S - \Sigma_j) - \frac{T_k^2}{2S^2} \Sigma_j (S - \Sigma_k) \end{aligned} \right\}. \quad (\text{A16})$$

The sums  $\sum_j$  whose limits are not explicitly stated extend from  $j=1$  to  $j=8$ . Here  $T_j = (S^2 - \Sigma_j^2)^{1/2}$ . Equations (A14) and (A16) are two alternative forms of writing  $a_C$  using restricted and unrestricted sums over  $n$ , respectively.

In Eq. (A12) the sum  $\sum_{(l,j)}$  is to be performed over the 24 nearest-neighbor links between the eight spins of the cluster ( $j$ ) and their corresponding three nearest-neighbor spins ( $l$ ) outside the cluster. In Eqs. (A14) and (A15) the sum  $\sum_{(j,k)}$  is to be performed over the 12 nearest-neighbor links between the eight spins of the cluster.

<sup>1</sup>K. W. Blazey and H. Rohrer, *Phys. Rev.* **173**, 574 (1968).

<sup>2</sup>K. W. Blazey, H. Rohrer, and R. Webster, *Phys. Rev.* **B 4**, 2287 (1971).

<sup>3</sup>J. Murphy and R. C. Ohlman, *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Wiley, New York, 1967), p. 239.

<sup>4</sup>K. W. Blazey and G. Burns, *Proc. Phys. Soc.* **91**, 640 (1967).

<sup>5</sup>J. S. Helman, R. A. Carvalho, H. Panepucci, M. C. Terrile, M. A. Aegerter, and E. Soarez, *Solid State Commun.* **31**, 1015 (1979).

<sup>6</sup>M. A. Aegerter, H. C. Basso, and H. J. Scheel (unpublished).

<sup>7</sup>J. S. Helman, *J. Phys. Chem. Solids* **32**, 251 (1971).

<sup>8</sup>Previously reported values (Refs. 3 and 4) for the exchange coupling constant in the excited state of Cr of 3.2 and 4.3  $\text{cm}^{-1}$  were obtained by interpreting a splitting seen in absorption as being entirely due to exchange. The splitting is actually almost temperature independent and may be related to crystal fields.

<sup>9</sup>H. Panepucci, M. C. Terrile, and M. Matsuoka (private communication).